

5           **USE OF TOCOPHEROL TO SCAVENGE ACETALDEHYDE IN  
              POLYETHYLENE TEREPHTHALATE CONTAINERS**

Claim of Priority

              This application claims priority from U.S. Provisional Patent  
Application Serial Number 60/511,455 bearing Attorney Docket Number  
10    12003018 and filed on October 15, 2003.

Field of the Invention

              This invention relates to use of a means to scavenge acetaldehyde in  
containers made from polyethylene terephthalate (PET).

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Background of the Invention

              Plastic has taken the place of other materials in a variety of  
industries. In the packaging industry, plastic has replaced glass to  
minimize breakage, reduce weight, and reduce energy consumed in  
20    manufacturing and transport.

              Polyethylene terephthalate (PET) is very often used as a plastic for  
replacement of glass in the packaging industry, particularly the beverage  
container industry.

              U.S. Pat. No. 5,874,517 (Huang et al.) discloses the problems in the  
25    art of regenerated acetaldehyde in PET resin and their method for solving  
that problem.

              As described in Huang et al., acetaldehyde is one of several  
byproducts created during PET polymerization, and remains in the  
polymer chip after polymerization is completed. Acetaldehyde must be  
30    minimized because it can introduce flavor to the drinks contained in the  
bottles, which is highly undesirable. The acetaldehyde trapped in the chip

during the polycondensation reaction to prepare PET, is widely known as "free" acetaldehyde. In addition to free acetaldehyde, acetaldehyde may also be formed by the further reaction or decomposition of PET and other byproducts ("acetaldehyde precursors") trapped in the polymer chip  
5 during polymer manufacture. Acetaldehyde produced from the reaction of trapped acetaldehyde precursors or which is formed during degradation occurring during the molding process is referred to as "regenerated" acetaldehyde. Reactions which produce regenerated acetaldehyde are induced when the polymer is subjected to high temperatures, such as  
10 those temperatures utilized in the injection molding process.

Huang et al. reports that antioxidants have been widely studied and used for preventing PET thermal and thermal oxidative degradation. But none reported by Huang et al. worked in order to reduce regenerated acetaldehyde while also maintaining color values acceptable for bottle  
15 resin.

U.S. Pat. No. 6,569,479 (Rule) discloses an oxidation catalyst active for the oxidation of acetaldehyde to acetic acid to be used in a beverage container.

## 20 Summary of the Invention

As Huang et al. stated, a need exists for a commercially acceptable PET resin which does not generate significant amounts of acetaldehyde when heated for molding into a container or bottle.

The present invention solves this problem but in a way unexpected  
25 by one of ordinary skill in the art, after taking into consideration the disclosures of Huang et al. and Rule.

One aspect of the present invention is a method of using DL-alpha-tocopherol to scavenge acetaldehyde from head space of a beverage container comprising polyethylene terephthalate.

Another aspect of the present invention is a polymeric container comprising compound comprising polyethylene terephthalate and an acetaldehyde scavenger comprising DL-alpha-Tocopherol.

A feature of the invention is the ability of DL-alpha-tocopherol to reduce concentration of acetaldehyde from head space of a beverage container containing a consumable beverage, especially one which has its taste affected by the presence of acetaldehyde in an enclosed beverage container.

An advantage of the invention is that commercial sources for DL alpha tocopherol readily exist and are otherwise approved for use with food.

Other features and advantages will become apparent in a review of the following embodiments.

## Embodiments of the Invention

### PET Resin

The terms "polyethylene terephthalate" and "PET" as used herein are used generally to include high-molecular weight polymers made by condensing ethylene glycol with dimethyl terephthalate or terephthalic acid no matter how prepared. Furthermore, these terms are meant to include well-known polyethylene terephthalate polymers which are modified by the inclusion of minor amounts, e.g., less than about 20 percent by weight of the polymer, of comonomers or modifying agents, as is otherwise well known.

Such comonomers or modifying agents include aromatic and aliphatic diols and polyols; aromatic and aliphatic carboxylic acids; or single molecules containing both carboxylic and alcohol functionality. Examples of diols include 1,4-butanediol, cyclohexanedimethanol, diethylene glycol and/or 1,3-propanediol. Examples of carboxylic diacids

include isophthalic acid, adipic acid, 2,6-naphthalene dicarboxylic acid and p-hydroxy benzoic acid. Minor amounts of chain branching agents and/or chain terminating agents may also be used. Such chain branching agents include, for example, polyfunctional acids and/or polyfunctional  
5 alcohols such as trimethylol propane and pentaerythritol. Chain terminating agents include monofunctional alcohols and/or monofunctional carboxylic acids such as stearic acid and benzoic acid.

Mixtures of chain branching and chain terminating agents may also be used. PET which contains such chain branching agents and chain  
10 terminating agents is described in U.S. Pat. No. 4,161,579.

The PET can be prepared by either a batch or continuous polymerization process by any means known to those having ordinary skill in this art. For example, PET can be prepared by the ester interchange (transesterification) of dialkyl esters of terephthalic acid such  
15 as dimethyl terephthalate or by the esterification of terephthalic acid with ethylene glycol.

PET reaction product can then be extruded at an elevated temperature into water and allowed to solidify therein. The solid PET can then be pelletized by means known to those skilled in this art. For  
20 example, the PET may be pelletized using an underwater pelletizer.

The PET useful in the present invention can in any form such as pellets, chips, granules, or powders, for further compounding and processing.

Alternatively, PET can be polymerized in a continuous process  
25 that includes an extrusion step at the end of the process.

The intrinsic viscosity of PET ranges from about 0.50 to about 1.0, preferably from about 0.65 to about 0.85 deciliters per gram based upon calculations made from measurements in o-chlorophenol at 25°C. The specific preferred range of intrinsic viscosity depends on end use.

A type of PET resin that may be of use in the present invention is that PET resin prepared according to the method disclosed in U.S. Pat. No. 5,874,517 (Huang et al.).

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#### Acetaldehyde Scavenger

The acetaldehyde scavenger is DL-alpha-Tocopherol. It is commercially available as antioxidant for plastics from BASF Corporation under the brands Uvinul® 2000 AO and Uvinul® 2003 AO.

10 As reported by BASF Corporation, Uvinul® 2000 AO is pure DL-alpha-Tocopherol, whereas Uvinul® 2003 AO is DL-alpha-Tocopherol modified by inclusion of an organophosphorus compound. Both are reported for use as inhibiting thermooxidative degradation.

15 DL-alpha-Tocopherol can be added to the PET resin in an amount ranging from about 1.25% to about 18%, and preferably from about 5% to about 16.7% weight percent of the total compound.

In the event that the compound is to be supplied to customers as a concentrate, the DL-alpha-Tocopherol can be added to the PET resin in an amount ranging from about 1.25% to about 18%, and preferably from  
20 about 5% to about 16.7% weight percent of the total compound acting as a concentrate.

Any conventional means to thoroughly mix the ingredients can be used in the present invention. Preferably, the ingredients are mixed using any conventional high intensity mixing apparatus without any special  
25 order of addition, at ambient temperature and sufficient mixing speed to thoroughly mix the ingredients.

In addition to the compound being available as a compound (fully "let-down") and a concentrate, the compound can be prepared for use in

the form of particulates according to the disclosure in U.S. Pat.  
Publication 20020198122 (Nitzsche).

It is unexpected that DL-alpha-Tocopherol functions as a  
scavenger for acetaldehyde. But proof of that function is found in the  
5 examples below.

#### Optional Ingredients

Any conventional polymeric additive can be considered for  
addition to compounds of the present invention. Non-limiting examples  
10 of such optional additives include slip agents, antiblocking agents,  
antioxidants, ultraviolet light stabilizers, quenchers, plasticizers, mold  
release agents, lubricants, antistatic agents, fire retardants, and fillers such  
as glass fibers, talc, chalk, or clay. Of these fillers, the properties of  
nanoclay can add stiffness, toughness, and charring properties for flame  
15 retardancy. Such optional additives can be included in the blend of the  
present invention in an amount from about 0 to about 40, and preferably  
from about 0.1 to about 30 weight percent. Most preferably, the amount  
is about 1 to about 7 weight percent of the blend.

Any conventional colorant useful in thermoplastic compounding is  
20 also acceptable for use in the present invention. Conventional colorants  
can be employed, including inorganic pigments such as titanium dioxide,  
iron oxide, chromium oxide, lead chromate, carbon black, silica, talc,  
china clay, metallic oxides, silicates, chromates, etc., and organic  
pigments, such as phthalocyanine blue, phthalocyanine green, carbazole  
25 violet, anthrapyrimidine yellow, flavanthrone yellow, isoindoline yellow,  
indanthrone blue, quinacridone violet, perylene reds, diazo red and others.  
The amount of colorant can range from none at all to about 4.0, and  
preferably from about 1.5 to about 2.0 weight percent of the total  
polymeric compound.

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### Usefulness of the Invention

Compound of PET and DL-alpha-Tocopherol according to the present invention can be used to produce containers such as PET beverage bottles for mineral water, carbonated liquids, white liquors, white wine,  
 5 and PET food containers for cheese.

Compounds containing PET and DL-alpha-Tocopherol according to the present invention can be molded into containers of various shapes by various means, including without limitation, reheat blow molding, injection blow molding, extrusion blow molding, and others known to  
 10 those skilled in the art.

It is reported by Huang et al. that bottle manufacturers specify acceptable levels of acetaldehyde based on measurements made in the bottle's head space subsequent to molding. Bottle head space acetaldehyde specifications are generally less than 4 µg/l for cola  
 15 beverages and less than 1 µg/l for water applications.

### Examples

PET bottles were prepared according to the recipes and commercial sources stated in Table 1 and the molding conditions stated in  
 20 Table 2.

<b>Table 1</b>					
<b>Recipes</b>					
<b>Ingredient Wt. %</b>	<b>Comp. Ex. A</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Uvinul 2000 AO	---	1.25%	5%	---	---
Uvinul 2003 AO	---	---	---	16.7%	6.7%
PET Polymer (0.8 I.V. Pellet)	40%	39.50%	38%	33.3%	37.3%
PET Polymer (0.8 I.V. Powder)	60%	59.25%	57%	50%	56.0%
<b>Commercial Sources</b>					
<b>Ingredient and Use</b>		<b>Source</b>		<b>Generic Name</b>	
Uvinul 2000 AO Acetaldehyde Scavenger		BASF		DL alpha Tocopherol	
Uvinul 2003 AO Acetaldehyde Scavenger		BASF		DL alpha Tocopherol	
PET Polymer (0.8 I.V. Pellet) Resin		GE		Polyethylene terephthalate	

Table 1		
PET Polymer (0.8 I.V. Powder) Resin	GE	Polyethylene terephthalate

Table 2					
Bottle Making Conditions					
Example	Comp. Ex. A	1	2	3	4
Compounding Equipment	Co-rotating Twin Screw Extruder				
Compounding Temperature	259°C Melt Temp				
Compounding Mixing Speed	250 rpm				
Molding Equipment	Aoki 100LL-20				
Mold Shape and Size	Boston Round 0.3mm wall thickness				
Molding Temperature	270°C-290°C				
Molding Injection Pressure	50 psi (0.344 mPa)				
Bottle Size	12 oz (354 ml)				

5           The bottles were fitted with an internal septa and capped with a bottle cap drilled to permit insertion of an acetaldehyde sampling tube. To sample the bottles, the serum cap was lanced with a knife and then the sampling tube was inserted through the hole in the bottle cap. A 3.1 mm hole was made near the bottom of the bottle to let air into the bottle while  
10 sampling. The industrial hygiene pump was turned on immediately upon placing the hole in the bottom of the bottle.

          Air (18 to 35 liters) was pulled through the bottles to sweep exhaustively the acetaldehyde into the sampling tube. The air exchanges compared to the bottle volume were well in excess of that needed to  
15 exchange the air volume.

Sampling Tube: SKC 226-119 (6mm by 110mm with two sections  
150/300 mg of DNPH coated silica gel)

Sampling Pump: SKC "Airchek Sampler" pump model 224-PCXR8

20 Sampling flow rate: nominal 0.4 to 0.5 liters/ min



Tube Preparation: Desorb front half and back half of sampling tube  
separately each with 3 mls of acetonitrile.

IH HPLC Method: (NIOSH 2016, modified for Acetaldehyde)

5 Instrument: Waters Model 2690 LC System

Column: Phenomenex LUNA C18 (4.6 by 50mm)

Column Temp: 30°C

Injection Volume: 15µl

Mobile Phase:

10 Phase A = 10:90 Acetonitrile:Water with 0.7708 g/L ammonium acetate

Phase B = 90:10: Acetonitrile:Water with 0.7708 g/L ammonium acetate

Flow rate: 0.75 ml/min

Gradient Program:

	Time, min	% A	%B	Curve
15	Initial	90	10	*
	4.0	38	62	6
	8.0	38	62	6
	10.0	90	10	6

20 Retention time acetaldehyde-DNPH derivative: 6.7 mins

Detection: UV at 360 nm

The interior spaces of PET bottles were sampled for acetaldehyde at two  
different intervals from sealing of the bottles on Day 1. On Day 11 for  
25 Examples 1 and 2 and Day 21 for Examples 3 and 4, the seals were  
removed from the bottles and were sampled for acetaldehyde presence  
using an exhaustive air exchange performed according to NIOSH Test  
No. 2016, described above to capture any acetaldehyde present in the  
head space of the bottle onto a sampling tube. As explained above, the

acetaldehyde was derivatized by dinitrophenylhydrazine (DNPH) coated onto silica gel. The tube was desorbed and the derivatized acetaldehyde was measured by High Performance Liquid Chromatography with UV detection at 360 nm.

5           Because the NIOSH method resulted in approximately 50-130 bottle volume exchange of air, a second sampling was possible. To do this, the bottles were then sealed shut. This was accomplished by taping the sampling air-inlet hole cut into the bottom of the bottle, with black electrical tape and capping the bottle top with a serum plug then bottle  
10 cap. The sealed bottles were placed within a plastic bag and stored on the lab countertop. They were kept in this condition until sampled in the second sampling.

          Due to the exhaustive air exchange used during the first testing, it was believed that all acetaldehyde released within the bottle up to that  
15 time was removed. Any acetaldehyde found in the second testing represented newly released acetaldehyde. The measurements were taken on Day 81 for Examples 1 and 2 and Day 91 for Examples 3 and 4.

          (This methodology cannot differentiate between "free" acetaldehyde originating from further release of entrapped acetaldehyde  
20 from initial bottle molding nor from "regenerated" acetaldehyde coming from any other mechanism (i.e. polymer degradation etc). This methodology does not measure any acetaldehyde released from the outer walls of the bottle to the environment.)

          Table 3 shows the results, an average of two samples for each  
25 Example 1-4 and the Comparative Example A.

Table 3					
Acetaldehyde Concentration (µg/l) in Head Space of Bottles					
	A	1	2	3	4
Day 11	3.42	1.55	0.99		
Day 21				1.34	1.06
Percent Improvement over Control	---	55%	71%	61%	69%
Day 81	2.47	0.61	0.44		
Day 91				0.73	0.60
Percent Improvement over Control	---	75%	82%	70%	76%

Table 3 shows that unexpected and dramatic improvement in minimizing acetaldehyde content in the head space of PET containers is possible by using pure DL-alpha-Tocopherol or modified with an organophosphorus compound. It is believed from the repetitive testing that such acetaldehyde scavenging will continue until the concentration of DL-alpha-Tocopherol is exhausted.

The invention is not limited to the above embodiments. The claims follow.